

高分子量的枝状聚硅烷的合成与表征*

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摘 要 根据硅氢加成反应机理设计了“顺点滴式”工艺,高效、低耗地合成了甲基苯乙基二氯硅烷和甲基正己基二氯硅烷.根据 Wurtz 还原偶联反应原理,采用“预聚”和“混聚”两种工艺分别合成枝状共聚硅烷,发现运用“预聚”工艺可以合成分子量很高的枝状聚硅烷.

关键词 枝状聚硅烷,顺点滴式,预聚,混聚

过去 30 年聚硅烷因其独特 Si—Si σ -共轭结构和特殊光电性质而备受注目,除可用作光致抗蚀剂、光致引发剂、波导器、光导体和非线性光学材料外^[1-3],还是制备 SiC、Si₃N₄ 等陶瓷的可溶或可熔前驱体^[4,5].聚硅烷的合成与性质一直是其研究的重点.

本文通过对多种硅氢加成反应工艺的比较研究,找到了高效、低耗合成甲基苯乙基二氯硅烷和甲基正己基二氯硅烷单体的方法,并利用它们与三氯甲基硅烷、三氯苯基硅烷作用合成了分子量很高的枝状聚硅烷.

1 实验部分

1.1 单体的合成

1.1.1 原料 苯乙烯,化学纯,使用前依次经 NaOH 溶液、水洗涤及无水 Na₂SO₄ 干燥后,减压蒸馏纯化;正己烯,化学纯,使用前经减压蒸馏纯化;二氯甲基硅烷,工业品,使用前经常压蒸馏纯化;双环戊二烯二氯化铂按文献[6]合成和纯化.

1.1.2 工艺 单体的合成工艺有 3 种:(1)在 250 mL 装配有温控系统、电磁搅拌系统、高纯氮气及尾气处理系统、恒压滴液漏斗和回流冷凝设备的三颈瓶中,在 0.2 L/min 高纯氮气保护下,将 0.3 mol 苯乙烯或正己烯与 1 mL (1 mg/mL) 双环戊二烯二氯化铂催化剂的 CH₂Cl₂ 溶液混和加热到合适温度并开始恒温,3~5 min 后以约 60 滴/min 速度滴入一定量二氯甲基硅烷,然后再回流 1 h 结束反应.减压蒸馏反应混合物,搜集相应温度范围馏分得产物.本文称为“顺点滴式”(Normal-

sequence-dripping mode). (2)与工艺(1)相同条件下,将二氯甲基硅烷与催化剂混和并加热至微沸,3~5 min 后滴入苯乙烯或正己烯,再在同(1)温度下恒温回流,称为“逆点滴式”(Opposite-sequence-dripping mode). (3)与工艺(1)相同条件下,将苯乙烯或正己烯与催化剂、二氯甲基硅烷完全混和加热到相应温度恒温回流,称为“全混式”(Fully-mixing mode).

1.2 聚合物的合成与表征

1.2.1 原料 甲基苯乙基二氯硅烷(MPES)和甲基正己基二氯硅烷(MHS)按 1.1 合成,使用前经减压蒸馏纯化;三氯甲基硅烷与三氯苯基硅烷,工业品,使用前经常压蒸馏纯化;金属 Na,分析纯;甲苯,化学纯,经金属 Na 回流干燥,使用前蒸出;乙二醇二甲醚等其他试剂为化学纯.

1.2.2 聚合物合成 聚合物均采用 Wurtz 还原偶联反应合成.投料程序有两种:(1)将二氯二取代硅烷和三氯硅烷的甲苯溶液混合后滴入钠砂与甲苯的混合物中加热回流 3 h,本文称为“混聚”(Mixed-polymerization). (2)先将二氯二取代硅烷甲苯溶液滴入钠砂与甲苯的混合物中加热回流 1 h,再滴入三氯硅烷的甲苯溶液进行接枝共聚 2 h,共 3 h,称为“预聚”(Pre-polymerization).

反应均以所用单体共含 0.2 mol 硅原子规模进行,金属 Na 根据单体含氯量,以过量 5 wt(%)计.基本操作和后处理方法与文献[7]相似,所得产物经真空烘干至恒重.

1.2.3 分析与表征 聚合物²⁹Si-NMR 和¹H-NMR 谱分别用美国 Unity 公司 Varian 200 型和 400 型核

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磁共振谱仪记录, CDCl₃ 溶剂, TMS 内标; 分子量及分布在美国 Water-486 型 GPC 仪上测定, 室温, 聚苯乙烯标样, THF 流动相; 紫外光谱由日本 Hitachi U-3500 型紫外吸收光谱仪记录, 环己烷溶剂, 溶剂参比.

2 结果与讨论

2.1 工艺对单体合成产率的影响

用日本 JNM-FX90Q 型核磁共振谱仪记录的产品 ¹H-NMR 谱表明, 苯乙烯硅氢加成产物甲基苯乙基二氯硅烷为 α 和 β 构型混合物, $\alpha : \beta = 45 : 55$; 1-己烯硅氢加成产物甲基正己基二氯硅烷主要为 β 构型.

从表 1 和表 2 可见, 所设计“顺点滴式”工艺可以明显提高反应产率, 这是因为在该实验条件下甲基二氯硅烷被烯烃单体与催化剂形成的过渡络合物(反应活化中心)很好地捕获并形成产物, 这与文献[8,9]论及的硅氢反应机理一致, 反应过程中基本无白烟也说明这一点. “全混式”由于反应过于剧烈, 导致反应物挥发过多而产率较低; “逆点滴式”因烯烃与 Pt 催化剂络合机会少导致活化中心较少而产率最低, 该工艺反应过程中尾气中始终出现大量白烟就说明这一点.

采用“顺点滴式”工艺还可以节约原料, 如 1-己烯硅氢加成, 在近沸腾温度下(约 55℃)反应, 即使甲基二氯硅烷用量减少, 平衡产率仍然很高, 在本实验条件下, 甲基二氯硅烷只需过量 10% 即可.

Table 1 Effect of the processes on the productivity of hydrosilylation with a 50% (vol) excess of dichloromethylsilane

Products	Reaction temperature	Normal -sequence -dripping mode	Opposite -sequence -dripping mode	Fully -mixing mode
MPES	82℃	87.9	82.0	82
MHS	70℃	84.8	69.5	80.1

Table 2 Effect of the dosages of dichloromethylsilane on the productivity of hydrosilylation of 1-hexylene using the process of “normal-sequence-dripping mode”

Dosage of dichloro-methylsilane (mL)	48	44	40	36	32
Excess (%)	50	37.5	25	12.5	0.0
Productivity	96.2	96.1	96.0	95.8	92.0

Reaction temperature: 55℃

2.2 聚合物的合成与表征

采用前述工艺, 本文设计并合成了四类枝状聚合物, 它们分别是甲基苯乙基二氯硅烷与三氯甲基硅烷、三氯苯基硅烷枝状共聚物 Polymethylphenethylsilene-co-methylsilyne (PMPES-co-MS) 与 Polymethylphenethylsilene-co-phenylsilyne (PMPES-co-PS), 以及甲基正己基二氯硅烷与三氯甲基硅烷、三氯苯基硅烷枝状共聚物 Polymethyl-*n*-hexylsilene-co-methylsilyne (PMHS-co-MS) 与 Polymethyl-*n*-hexylsilene-co-phenylsilyne (PMHS-co-PS), 其合成方法、原料配比、产率以及部分重要性质见表 3~8.

Table 3 Characterization of poly(methylphenethylsilene-co-methylsilyne)s derived from mixed-polymerization without diglyme

Sp	Monomer feed ratio: D/T (mol)	Appearance (25℃)	M_w (M_w/M_n)	Yield (%)	UV Absorption λ_{max} (nm)	Band assignment	Absorption edge (nm)
B1	0.200/0 (10/0)	Whitish sticky solid	58300 (4.9)	43.9	220 301	Ph- π - π^* Si-Si σ - σ^*	< 380
B2	0.182/0.018 (10/1)	Yellowish sticky solid	17600 (2.1)	89.9	238.7	Branching broad	368
B3	0.167/0.033 (5/1)	Yellow sticky solid	14500 (1.4)	62.5	230.1	Branching broad	354
B4	0.150/0.050 (3/1)	Yellow sticky solid	10100 (1.6)	55.4	228.3	Branching broad	369
B5	0.133/0.067 (2/1)	Yellowish-brown	4600 (4.6)	45.7	222	Branching broad	373
B6	0.100/0.100 (1/1)	Yellowish-brown solution	No data	29.8	228.3	Branching broad	428
B7	0/0.200 (0/10)	Yellow insoluble solid	No data	90/ 15 h	No peak	Branching broad	> 430

Table 4 Characterization of poly(methylphenethylsilene-co-methylsilyne)s derived from pre-polymerization without diglyme

Sp	Monomer feed ratio: D/T(mol)	Appearance (25℃)	M_w (M_w/M_n)	Yield (%)	UV Absorption λ_{max} (nm)	Band assignment	Absorption edge(nm)
Ba	0.182/0.018(10/1)	Yellowish sticky solid	11000 (4.4)	31.8	212.3 298.9	Ph- π - π^* Si-Si σ - σ^*	339
Bb	0.167/0.033(5/1)	Yellowish sticky solid	243400 (10.8)	28.4	212.5	Branching broad	440
Bc	0.150/0.050(3/1)	Yellowish sticky solid	283500 (7.5)	33.3	213.1	Branching broad	466
Bd	0.133/0.067(2/1)	Yellowish sticky solid	146600 (9.3)	29.5	214.6	Branching broad	423
Be	0.100/0.100(1/1)	Whitish sticky solid	36000 (8.6)	34.0	215.1	Branching broad	400

Table 5 Characterization of poly(methylphenethylsilene-co-methylsilyne)s prepared with 15% diglyme by volume

Sp	Monomer feed ratio: D/T(mol)	Synthesis procedure	Appearance (25℃)	M_w (M_w/M_n)	Yield (%)	UV Absorption λ_{max} (nm)	Band assignment	Absorption edge(nm)
B-1	0.182/0.018 (10/1)	Mixed-polymn	White waxy solid	2200 (2.0)	70.4	237.9	Branching broad	337
B-2	0.167/0.033 (5/1)		Yellowish sticky solid	1500 (1.7)	67.4	229	Branching broad	339
B-3	0.100/0.100 (1/1)	Mixed-polymn	Yellow waxy solid	8700 (1.8)	56.5	218.5	Branching broad	382
B-4	0.182/0.018 (10/1)	Pre-polymn	Yellowish sticky solid	26100 (6.2)	71.1	217.3 298.7	Ph- π - π^* Si-Si σ - σ^*	449

Table 6 Characterization of poly(methylphenethylsilene-co-phenylsilyne)s prepared with 15% diglyme by volume

Sp	Monomer feed ratio: D/T(mol)	Synthesis procedure	Appearance (25℃)	M_w (M_w/M_n)	Yield (%)	UV Absorption λ_{max} (nm)	Band assignment	Absorption edge(nm)
C1	0.182/0.018 (10/1)	Mixed-polymn	White waxy solid	5000 (2.8)	76.1	217.9 296.3	Ph- π - π^* Si-Si σ - σ^*	343
C2	0.167/0.033 (5/1)	Mixed-polymn	Yellowish sticky solid	3500 (1.4)	73.8	217.7	Branching broad	360
C3	0.150/0.050 (3/1)	Mixed-polymn	Yellowish sticky solid	2100 (2.3)	68.3	217.5	Branching broad	368
C4	0.133/0.067 (2/1)	Mixed-polymn	Yellow waxy solid	2000 (1.6)	64.6	219.1	Branching broad	381
C5	0.100/0.100 (1/1)	Mixed-polymn	Yellow waxy solid	1600 (1.3)	61.3	225.9	Branching broad	388
C6	0/0.200 (0/10)		Yellow solid	900 (1.73)	37.2/ 15 h	< 266	Branching broad	410
C7	0.182/0.018 (10/1)	Pre-polymn	Yellowish waxy solid	24400 (4.5)	69.1	218.3 299.3	Ph- π - π^* Si-Si σ - σ^*	462

2.2.1 产率 从表 3~8 可知,在本实验条件下,通过“混聚”方法合成的可溶性枝状共聚物产率(28.4%到 89.9%)明显高于相同条件下的均聚物产率(PMPES 为 43.9%,PMHS 为 25.5%),特别是配料比 D/T(二氯硅烷/三氯硅烷)较大时更是如此,这与前人合成线性共聚硅烷所得到的结论相似^[1,7].但随着 D/T 值减小,可溶性枝状共聚物的产率有所下降.通过“预聚”方法合成枝状共聚物时,在同样条件下,产率比“混聚”方法低.

对于“混聚”工艺,正如 Akira Watanabe 等^[10-13]所报道的那样,由于各种有机官能团(如

苯乙基,正己基等)与枝化时形成的二维 Si-骨架网状聚硅烷 Polymethylsilylene 或 Polyphenylsilylene 等支链的较强空间位阻,在聚合物骨架上枝化会很困难.因此,当 D/T 值较大时,由于枝化时形成的二维 Si-骨架网状聚硅烷 Polymethylsilylene 或 Polyphenylsilylene 等支链较少,它们在聚合物链上结合较为容易,枝化产物产率较高.反之,如 D/T 值较小时,枝化时形成的二维 Si-骨架网状聚硅烷 Polymethylsilylene 或 Polyphenylsilylene 等支链较多,它们在聚合物链上结合较为困难,枝化产物产率会较低.

Table 7 Characterization of poly(methyl-*n*-hexylsilylene-co-methylsilylene)s prepared without diglyme

Sp.	Monomer feed ratio; D/T(mol)	Synthesis procedure	Appearance (25℃)	M_w (M_w/M_n)	Yield (%)	UV Absorption λ_{max} (nm)	Band assignment	Absorption edge(nm)
C③	0.182/0.018	Mixed-polymn	Yellowish sticky solution	No data	71.9	213.5 301.5	Unclear Si-Si $\sigma-\sigma^*$	339
C⑥	0.167/0.033	Mixed-polymn	Yellowish sticky solution	No data	50.9	212.7 297.3	Unclear Si-Si $\sigma-\sigma^*$	350
C⑦	0.100/0.100	Mixed-polymn	Yellow sticky solution	17000 (8.1)	42.1	212.3	Branching broad	392
C⑩	0/0.200		Yellow solid	No data	No data	No peak	No data	No data
C⑪	0.182/0.018	Pre-polymn	Yellowish solid	63200 (19.2)	76.1	211.5 306.9	Unclear Si-Si $\sigma-\sigma^*$	428

Table 8 Characterization of poly(methyl-*n*-hexylsilylene-co-phenylsilylene)s prepared without diglyme

Sp.	Monomer feed ratio; D/T(mol)	Synthesis procedure	Appearance (25℃)	M_w (M_w/M_n)	Yield (%)	UV Absorption λ_{max} (nm)	Band assignment	Absorption edge(nm)
C①	0.200/0		Whitish sticky solid	70900 (27.4)	25.5	211.5 306.9	Unclear Si-Si $\sigma-\sigma^*$	342
C②	0.182/0.018	Mixed-polymn	Yellowish sticky solution	No data	80.2	212.1 303.3	Ph- $\pi-\pi^*$ Si-Si $\sigma-\sigma^*$	349
C③	0.167/0.033	Mixed-polymn	Yellowish sticky solution	No data	82.6	231.1 297.9	Ph- $\pi-\pi^*$ Si-Si $\sigma-\sigma^*$	429.9
C④	0.100/0.100	Mixed-polymn	Yellow-brown sticky solid	2700 (1.5)	78.5	222.3	Branching broad	401
C⑤	0/0.200		Yellow-brown solid	900 (1.73)	No data	No data	No data	No data
C⑥	0.182/0.018	Pre-polymn	Yellowish sticky solid	29900 (11.3)	64.7	211.3 306.1	Ph- $\pi-\pi^*$ Si-Si $\sigma-\sigma^*$	470

而对于“预聚”工艺,枝化时随着三氯硅烷的加入,反应形成的线性均聚物 PMPES 或者 PMHS 高分子链受到不断增长的硅烷阴离子链“回嵌”反

应^[11]影响而断裂,一部分分子来不及枝化而形成热力学稳定性很好的低分子量环状寡聚物(通常为五元环或六元环)从而失去枝化和聚合能力^[1],

因此这类枝状聚硅烷产率较低.

由于溶剂效应,使用催化剂二乙二醇二甲醚时,枝化产物产率比不使用时高.这和合成线性聚硅烷情况相似^[1].

2.2.2 GPC 通过“混聚”工艺形成的枝状共聚硅烷分子量通常较低(通常小于 10^4 ,肯定比相同条件下的线性均聚物分子量低),且随着 D/T 值减小而减小,这和前人的工作是一致的^[11].如果枝化时使用一些(如按 15% 体积比加入)二乙二醇二甲醚催化剂,枝化产物分子量下降更明显.

但是,运用“预聚”工艺枝化形成的共聚物分子量比通过“混聚”工艺形成的枝状共聚物分子量大得多,甚至比相同条件下的均聚物高,即使使用二乙二醇二甲醚催化剂时,“预聚”产物分子量仍然高于 10^4 .而且,两种枝状共聚硅烷的分子量随 D/T 值的变化也完全不同.随着 D/T 值减小,“预聚”产物分子量先增加后减小.

两种枝状共聚物分子量分布也不同.“混聚”产物多分散系数通常较小,使用二乙二醇二甲醚催化剂后会更小;“预聚”产物多分散系数通常较大,表现出分子量多分散特性.

从上节讨论可知,高分子链上有机官能团和环(网)状硅烷侧基很大,当在高分子链上它们之间距离很小时,或者说高分子枝化点密度很大时,这些基团之间的空间位阻会很大,形成高分子量的枝状共聚物会很困难.

对于“混聚”工艺,随着 D/T 值减小,反应中形成的环(网)状硅烷支链越多,空间位阻越大,不断增长的硅烷阴离子链“回嵌”反应会更容易导致高分子链断裂,高分子量的枝状共聚物更难形成.由于高分子链的这种增长和断裂同时发生,“混聚”产物的分子链长度会更趋一致,分子量多分散系数减小.

如果使用二乙二醇二甲醚催化剂,溶剂效应

使高分子链缩短,在相同条件下所得枝状高聚物分子量会更小.

而对于“预聚”工艺,由于二氯硅烷单体预先均聚形成了较长的线性高分子链,当 D/T 值较大时,随着三氯硅烷的加入,有足够的空间让环(网)状硅烷支链在硅烷阴离子链的“回嵌”反应过程中结合到聚合物 Si—Si 链上去形成高分子量聚合物.此时,随着 D/T 值减小,聚合物链上结合中环(网)状硅烷支链越多,产物分子量越大.但当 D/T 值很小时,反应体系中形成的环(网)状硅烷基团很多,空间位阻很大,硅烷阴离子链“回嵌”反应使聚合物分子断裂占优势,产物分子量会较小;而随着 D/T 值不断增大,分子量反而增大.正是由于硅烷阴离子链的“回嵌”反应,“预聚”工艺下的反应体系中,会出现较多的低分子量产物,因此这种产物分子量分布较宽,多分散性系数较大.但其多分散性系数通过多次溶解、结晶可适当减小.

2.2.3 紫外光谱 聚硅烷特殊的紫外光谱是其高分子 Si—Si 链 σ -电子离域作用的结果^[1],它与聚合物分子量^[14]、形态^[15]、取代基类型^[16]等有关.

枝状共聚硅烷的紫外吸收光谱与线性均聚物、线性共聚物都明显不同.线性聚硅烷通常在 300 到 350 nm 表现出强的吸收峰,这是 Si—Si σ - σ^* 吸收的结果;随着取代侧基的不同,也可能出现其他吸收峰.枝状共聚硅烷在 300 到 350 nm 处不一定有强的吸收峰,通常随着反应体系中三氯硅烷增多,枝状共聚硅烷在 300 到 350 nm 处 Si—Si σ - σ^* 吸收谱带会逐渐减弱并发生兰移,甚至会完全消失.一些取代基的吸收峰会随反应体系中三氯硅烷增多而增强,有时取代基吸收峰会和 Si—Si σ - σ^* 吸收峰混在一起形成一个宽波带而难于区分.图 1~4 是部分样品紫外吸收谱图,其结果与 Watanabe 等^[11]合成的枝状共聚硅烷极其相似(参见表 3~8).

Table 9 ¹H-NMR chemical shifts for typical polysilanes(1)*

Sample	B1	B5	B-4	C2	C7
Monomer feed ratio: D/T(mol)	10:1	2:1	10:1	5:1	10:1
Synthesis procedure		Mixed polymn	Pre-polymn	Mixed polymn	Pre-polymn
Si—CH ₃	0.266(b)	0.307(vb)	0.333(vb)	0.362(b)	0.333(b)
Si—CH ₂ —	1.432(vb)	1.486(b)	1.483(vb)	1.494(b)	1.342(b)
Ph—CH ₂ —	2.585(b)	2.675(b)	2.617(b)	2.610(b)	2.614(b)
Ph—	7.145(ms)	7.168(ms, vb)	7.066(ms, b)	7.066(ms, vb)	7.120(ms, b)
Co-polymn ratio: D/T(mol)		2.8:1	8.7:1	5.25:1	4.23:1

* (b) broad, (m) multiple, (s) sharp, (v) very, (w) weak

Table 10 ¹H-NMR chemical shifts for typical polysilanes(2)*

Sample	C①	C②	C③	C④	C⑤
Monomer feed ratio: D/T(mol)	0.200:0	1:1	10:1	5:1	10:1
Synthesis procedure		Mixed polymn	Pre-polymn	Mixed polymn	Pre-polymn
Si—CH ₃	0.243(m, b)	0.087(m, b)	0.243(m)	0.241(vb)	0.240(m, b)
Si—CH ₂ —	0.729(b)	0.728(vb)	0.830(b)		0.832(b)
(CH ₂) ₄ —CH ₃	0.888(m)	0.886(s)	0.887(s)	0.870(b)	0.886(m, s)
CH ₃ —(CH ₂) ₄	1.284(m)	1.280(s)	1.304(s)		1.281(m, s)
Ph-				7.292(vb)	
Co-polymn ratio: D/T(mol)		1.76:1	8.9:1	1.5:1	

* (b) broad, (m) multiple, (s) sharp, (v) very, (w) weak

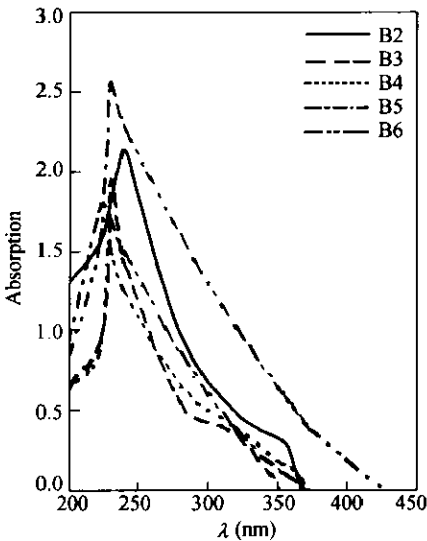


Fig. 1 Absorption spectra of cyclohexane solutions of PMPES-co-MS derived from the mixed-polymerization procedure without diglyme

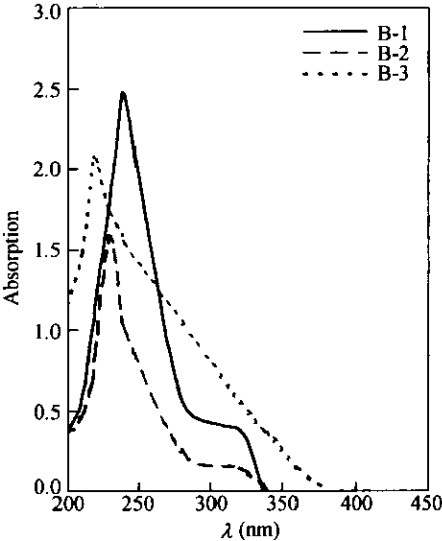


Fig. 3 Absorption spectra of cyclohexane solutions of PMPES-co-MS derived from the mixed-polymerization procedure with 15% diglyme

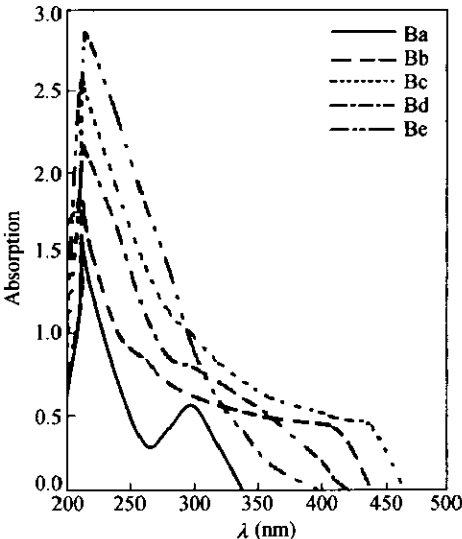


Fig. 2 Absorption spectra of cyclohexane solutions of PMPES-co-MS derived from the pre-polymerization procedure without diglyme

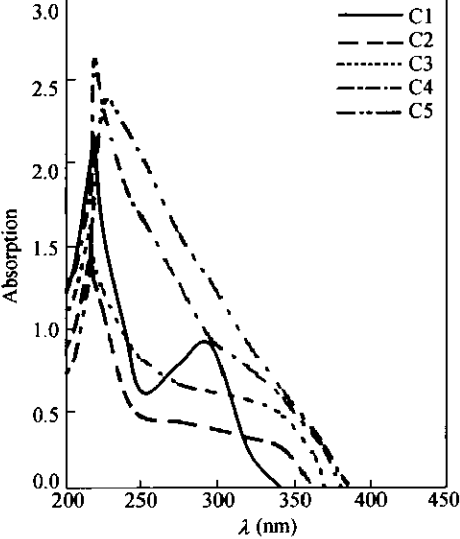


Fig. 4 Absorption spectra of cyclohexane solutions of PMPES-co-MS derived from the mixed-polymerization procedure with 15% diglyme

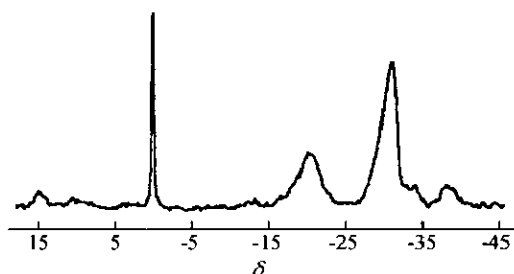


Fig. 5 ^{29}Si -NMR spectra of typical branched copolysilane C7

2.2.2.4 ^1H -NMR 谱 图 5 是典型样品的 ^{29}Si -NMR 谱, 其中化学位移 14.883 和 10.509 分别归属端基 $-\text{SiMe}(\text{CH}_2\text{CH}_2\text{Ph})$ 和 $-\text{SiOMe}(\text{CHMePh})$ 结

硅原子, -20.479 和尖峰 -31.083 分别归属 $-\text{SiMe}(\text{CH}_2\text{CH}_2\text{Ph})$ 和 $-\text{SiMe}(\text{CHMePh})$ 基硅原子, -34.150 和宽峰 -38.429 分别归属 $-\text{SiOMePh}$ 和 $-\text{SiPh}-$ 基硅原子; 表 9 和表 10 是部分样品的 ^1H -NMR 谱分析结果. 这些信息显示所合成产物为枝状共聚硅烷. 但是, 必须指出的是, 采用不同聚合工艺, 所得产物共聚比与投料比不完全一致, 这与 Watanabe 等^[11] 工作不同. 在作者的实验中, 发现当采用“混聚”工艺时, 枝状共聚硅烷的实际共聚比(D/T)比投料比低; 而采用“预聚”工艺时, 枝状共聚硅烷的实际共聚比比投料比高. 考虑到 2.2.1 和 2.2.2 节的讨论, 这种现象的出现应该是合理的.

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SYNTHESIS AND CHARACTERIZATION OF BRANCHED COPOLYSILANES OF HIGH MOLECULAR WEIGHT

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Abstract According to the mechanism of hydrosilylation, the process of “normal-sequence-dripping mode” was designed. And using such process, the monomers of dichloromethylphenethylsilane and dichloromethyl (*n*) hexylsilane were synthesized with high productivity (the maximal productivity of dichloromethylphenethylsilane, 88%, and dichloromethyl-*n*-hexylsilane, 96.2%) and low pollution (minute quantity of fumes in off-gas). By Wurtz reductive coupling reaction of dichlorosilane (dichloromethylphenethylsilane and dichloromethyl (*n*) hexylsilane) and trichlorosilane (trichloromethylsilane and trichlorophenylsilane), four series of two-dimensionally branched copolysilanes were designed and synthesized using the two procedures of “pre-polymerization” and “mixed-polymerization” with or without diglyme. The polymers are polymethylphenethylsilene-*co*-methylsilynes, polymethylphenethylsilene-*co*-phenylsilynes, polymethyl-*n*-hexylsilene-*co*-methylsilynes, and polymethyl-*n*-hexylsilene-*co*-phenylsilynes. Through the characterization of GPC, UV, ¹H-NMR and ²⁹Si-NMR, the properties of such copolysilanes were determined. The effects of such factors as monomer characteristics, co-polymerization ratio (D/T), co-polymerization mode (“pre-polymerization” and “mixed-polymerization”), solvent additive (diglyme) and reaction time on the polymer properties, such as productivity, molecular weight and UV absorption spectra, were studied and discussed. It was discovered that the branched copolysilanes of very high molecular weight with highly bulky substituents could be obtained with “pre-polymerization”. The maximum of the molecular weight of such branched copolysilanes could reach 2.8×10^5 , which was at least ten times as those of the branched copolysilanes derived from the mixed-polymerization procedure. The mechanism of increasing the molecular weights of branched copolysilanes was proposed.

Key words Branched copolysilane, Normal-sequence-dripping mode, Pre-polymerization, Mixed-polymerization